Halfwidths and line center shifts in diatomic molecules under strong vibrational excitation

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The influence of the vibrationally dependent factors of intramolecular dynamics on HF and CO relaxation parameters under conditions of strong vibrational excitation has been investigated. Calculation model has been developed, which takes into account variations of functions of dipole and quadrupole moments and polarizability under the influence of strong vibrational excitation. The calculational results for the vibrational dependence of halfwidths and line center shifts are presented for HF–HF (up to v = 22) and CO–CO (up to v = 50) of cold and hot bands.

Introduction

Study of excited molecular gaseous media calls for spectral line parameters like broadening coefficients and line center shifts. For example, CO lasers generate at cascade transitions when exciting up to 30–40 vibrational quanta;[1] the HF lasers also generate at high vibrational transitions. Therefore, it is desirable to estimate the influence of the radiation-absorbing molecule vibrational excitation on the above-mentioned relaxation parameters.

Earlier, the halfwidths and line center shifts have been measured up to v = 2 for the HF molecule[2–5] and up to v = 3 for the CO one.[6–8] At present, experimental or calculated values of halfwidths and line center shifts generated by transitions to highly excited vibrational states are not available in literature.

As is known, vibrational excitation can significantly change molecular parameters, e.g. dipole and quadrupole moments and the polarizability, which determine intermolecular interactions, therefore, variations in broadening coefficients and line shifts should be expected. Besides, the vibrational excitation changes the structure of rotational energy spectrum; this can also result in frequency variations and changes in probabilities of collision-induced transitions and, hence, cause variations in halfwidths and line shifts. At the same time, specific effects of the theory of spectral line collisional broadening can appear connected with vibrational dependence of adiabatic shift of levels at collisions. As is shown in Ref. 9, such effect widens H_2O halfwidths in bands caused by excitation of valence vibrations. In molecules of H_2O-type, halfwidth losses are to be expected in bands of the $n\nu_2$-type, connected with excitation of “soft” bending vibration.[10]

Thus, the preliminary analysis has shown that different factors of the rovibrational interaction can influence line relaxation parameters in different ways, increasing or decreasing them. Emphasize, that necessary data on the influence of the mentioned parameters of intermolecular interaction on halfwidths and line center shifts are lacking for today. Even the direction of line halfwidth variations is unknown.

The purpose of this work is to study halfwidths and line center shifts generated by transitions to highly excited vibrational states of diatomic molecules with different types of chemical bonds, i.e. HF (ionic bond) and CO (covalent one). Estimates of the influence of the vibrational dependence of dipole and quadrupole moments, polarizability, and rotational constant on halfwidths and line center shifts of higher rovibrational HF and CO bands under self-broadening conditions are presented.

1. Theoretical study

The traditional way of determining rovibrational energy levels and wave functions is the use of the perturbation theory (commonly, the effective rotational Hamiltonian method). The principal assumption of the perturbation theory is a smallness of the intermolecular interactions energy in comparison with the energy of zero-order approximation. As the latter, the harmonic oscillator is taken, when all parameters, e.g. dipole moment, potential energy function or the moment of inertia are presented as the Taylor expansions near the molecule equilibrium configuration. Mean values of molecular parameters are also presented as expansions in powers of vibrational quantum numbers, as a rule, limited by two first expansion terms.

Vibrational wave functions for moderately excited vibrational states are localized in a small neighborhood of the equilibrium configuration. Consequently, average values of dipole and quadrupole moments, as well as the polarizability, determining intermolecular potential, vary insignificantly when exciting one or several vibrational quanta. Variations of average values of multipole moments, as well as of rotational and centrifugal constants, rotational energy spectrum can be easily accounted in terms of the perturbation theory.

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Absolutely another situation should be expected under strong vibrational excitation. In this work, a Morse oscillator model was used to determine the potential function. Morse potential parameters for HF and CO were determined through fitting to an *ab initio* calculated potential function. Figure 1 shows the potential-energy function (PEF) for HF molecule, energy levels and wave functions for the ground (v = 0) and several highly excited (v = 5, 10, 15, 22) vibrational states, as well as functions of dipole and quadrupole moments and the polarizability, *ab initio* calculated in Refs. 11–13. The dissociation limit of the HF molecule is 49 000 cm^{-1}, the Morse potential maintains 22 vibrational states.

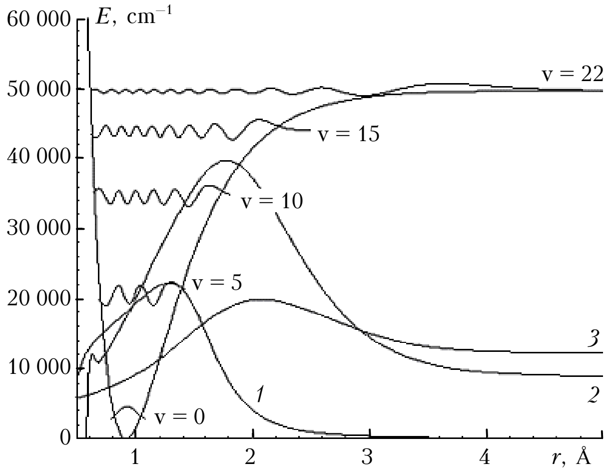

Fig. 1. PEF and wave functions (v = 0, 5, 10, 15, 22) of HF molecule: dipole-moment function ($\times 10^4$ D) (*1*); quadrupole-moment function ($\times 10^4$ D · Å) (*2*); and polarizability function ($\times 10^4$ Å^3) (*3*).

As can be seen, the ground-state wave function is localized in a small neighborhood of the equilibrium configuration, while wave functions of highly excited states (v = 10, 15, 22) cover a vast area overlapping the most part of the range of the dipole moment variation. Such a large amplitude of the atom vibration evidently requires taking into account the behavior of HF dipole-moment and polarizability functions at $r \to 0$ and $r \to \infty$. At $r \to 0$, the mean dipole moment tends to the dipole moment of the united atom; at $r \to \infty$ (molecule dissociation) the HF molecule dipole moment tends to 0. The same behavior is observed for the quadrupole moment and the mean dipole polarizability. The HF molecular properties at $r \to 0$ and $r \to \infty$ are discussed in Ref. 14 in more detail.

The Table below presents the distance between the turning points Δr, the rotational constant B, and the mean values of the dipole moment μ, quadrupole moment q, and polarizability α for different values of the vibrational quantum number v.

It is seen that the rotational constant decreases by a factor of 7 at v = 22, while the dipole moment decreases by a factor of 8 as compared to the values at its ground state. The distance between turning points increases 12 times totally overlapping variation ranges of dipole and quadrupole moments and the polarizability.

HF and CO intramolecular characteristics in excited vibrational states

v	Δr, Å	B, cm^{-1}	μ, D	q, D · Å	α, Å^3
			HF		
0	0.2	20.62	1.83	2.38	0.780
5	0.7	17.93	1.969	2.219	0.999
10	1.1	14.11	1.776	2.862	1.276
15	1.7	10.16	1.092	3.254	1.598
22	2.4	2.96	0.228	1.736	1.490
			CO		
0	0.12	1.92	−0.11	−2.0	1.940
5	0.28	1.85	−0.009	−1.846	2.021
10	0.45	1.77	0.120	−1.699	2.102
20	0.72	1.595	0.386	−1.339	2.289
30	0.92	1.41	0.658	−0.855	2.510
40	1.03	1.22	0.906	−0.176	2.756
50	1.12	1.018	1.042	0.842	2.968

Another situation is observed for CO molecule (Fig. 2, Table). Its dissociation limit is 89 500 cm^{-1}, the potential function maintains 83 vibrational states. Though the distance between wavefunction turning points near the dissociation limit increases significantly (14 times) only a small part of functions of dipole and quadrupole moments and polarizability is overlapped.[15–17] When calculating relaxation parameters of CO lines, this part is to be taken into account, disregarding their asymptotic behavior at $r \to \infty$ and $r \to 0$.

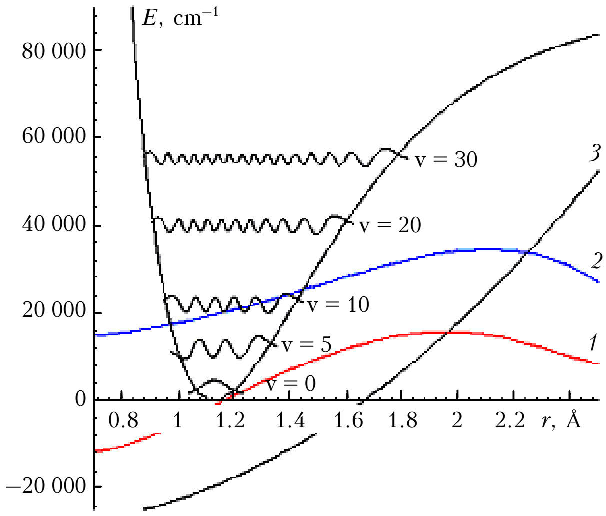

Fig. 2. Potential function (cm^{-1}) and wave functions of v = 0, 5, 10, 20, 30 states of CO molecule: dipole-moment function ($\times 10^4$ D) (*1*); polarizability function ($\times 10^4$ Å^3) (*2*); and quadrupole-moment function ($\times 10^4$ D · Å) (*3*).

Thus, line broadening of diatomic molecules at highly excited states is determined by variations of matrix elements of multipole moments and the polarizability, as well as by the dependence of rotational and centrifugal constants on the vibrational quantum number v near the dissociation limit. The

Table data show that significant changes in halfwidths and line center shifts, generated by transitions to highly excited vibrational states, are to be expected.

2. Results and discussion

In the context of one of the versions of semiclassical impact theory,[18] in the approximation of straight-line paths and mean collision velocity, the line halfwidth $\gamma(i, f)$ is expressed as

$$\gamma(i,f) = \frac{nv}{c}\sum_j \rho(j) \times$$

$$\times \int_0^\infty \left[1 - \exp\left\{-\mathrm{Re}\,S_2^{\mathrm{outer}}(b)\right\}\cos\left\{S_1(b) + \mathrm{Im}\,S_2^{\mathrm{outer}}(b)\right\}\right] b\,db. \tag{1}$$

Here n is the concentration of perturbing particles; v is the mean relative velocity of a molecule; c is the light speed; $\rho(j)$ is the population of the rotational level j; $\mathrm{Re}S_2(b)$ and $\mathrm{Im}S_2(b)$ are the real and imaginary parts of the effectiveness function of the 2nd order, $S(b) = iS_1(b) + S_2^{\mathrm{outer}}(b) + iS_2^{\mathrm{outer}}(b) + \ldots$.

The real part of the effectiveness function of the 2nd order is

$$\mathrm{Re}\,S_2^{\mathrm{outer}}(i,f,b,v) = \frac{4}{9}\frac{1}{(\hbar v b^2)^2}\sum_{j'} D(jj' \mid 1) \times$$

$$\times \left\{\sum_{i'} D(ii' \mid 1)\mathrm{Re}\,\varphi_{11}(k_{ii'jj'}) + \sum_{f'} D(ff' \mid 1)\mathrm{Re}\,\varphi_{11}(k_{ff'jj'})\right\}, \tag{2}$$

where $\varphi_{11} = \mathrm{Re}\varphi_{11} + i\mathrm{Im}\varphi_{11}$ is the complex resonance function for the dipole–dipole interaction. The summarized strength D of the line is determined as the product of the squared matrix element of the dipole moment μ of an absorbing molecule in the vibrational state i or f and the Clebsch–Jordan coefficient.[19] The cold-transition line strength depends on the diagonal matrix element of the dipole moment:

$$D(ii' \mid 1) = \left|\langle V_i|\mu|V_i\rangle\right|^2 (i100 \mid i'0)^2. \tag{3}$$

Here $|V_i>$ is the vibrational wave functions of the initial transition state; $(i100|i'0)$ are the Clebsch–Jordan coefficients,[19] $i = 0, \ldots, 22$. The strength of a hot-transition line depends on the off-diagonal matrix element of the dipole moment:

$$D(ii' \mid 1) = \left|\langle V_i|\mu|V_{i+1}\rangle\right|^2 (i100 \mid i'0)^2. \tag{4}$$

The resonance parameter k in Eq. (2) is determined by the energy balance of rotational levels in upper and ground vibrational states:

$$k_{ii'jj'} = \frac{2\pi cb}{v}(E_i - E_{i'} + E_j - E_{j'}) = \frac{2\pi cb}{v}(\omega_{ii'} + \omega_{jj'}). \tag{5}$$

Replacing indices i, i' by f, f', the resonance parameter $k_{ii'jj'}$ in the upper vibrational state of the transition can be obtained.

Let us use the average transition frequency approximation,[14] where the resonance function depends on mean values of transition frequencies in Eq. (5). Let $\bar{\omega}_{ii'}$, $\bar{\omega}_{ff'}$, $\bar{\omega}_{jj'}$ be the mean values of virtual transition frequencies. Use them in calculating the $\mathrm{Re}S_2^{\mathrm{outer}}(i, f, b, v)$ function in Eq. (2). Let C_i denote the resonance function values, calculated with mean frequencies for the ground vibrational state, while C_f – for the upper one:[14]

$$\begin{aligned} \mathrm{Re}\varphi_{11}\left[\frac{2\pi cb}{v}(\bar{\omega}_{ii'} + \bar{\omega}_{jj'})\right] &= C_i(b,B_i), \\ \mathrm{Re}\varphi_{11}\left[\frac{2\pi cb}{v}(\bar{\omega}_{ff'} + \bar{\omega}_{jj'})\right] &= C_f(b,B_f). \end{aligned} \tag{6}$$

When Eq. (6) is used for calculating the effectiveness function (2), the summation over i', f', and j' is contracted to the squared average dipole moment of an absorbing or perturbing molecule. As a result, we obtain a quite simple approximation for $\mathrm{Re}S_2^{\mathrm{outer}}$:

$$\mathrm{Re}\,\tilde{S}_2^{\mathrm{outer}}(i,f,b,v) =$$

$$= \frac{4}{9}\frac{1}{(\hbar v b^2)^2}\mu_0^2\left\{\mu_i^2 C_i(b,B_i) + \mu_f^2 C_f(b,B_f)\right\}; \tag{7}$$

where

$$\mu_2^2 = \left|\langle 0|\mu_2|0\rangle\right|^2, \quad \mu_i^2 = \left|\langle i|\mu_1|i\rangle\right|^2, \quad \mu_f^2 = \left|\langle f|\mu_1|f\rangle\right|^2.$$

The approximation of the mean transition frequency in Eq. (7) allows accounting for the influence of the dipole moment and rotational constant variations caused by an increase of the atom vibration amplitude in the absorbing molecule at the vibrational excitation. Mean frequencies of virtual transitions in Eq. (6) were calculated as

$$\bar{\omega}_{ff'} = 2B_f + 2Bj_{\max}. \tag{8}$$

Here B_f is the rotational constant of the absorbing molecule in the upper vibrational state of transition; $j_{\max}$ is the rotational quantum number for the most populated level of the perturbing molecule ($j_{\max} = 4$ for HF molecule according to calculations of the density matrix $\rho(j)$). Such a choice of mean transition frequencies corresponds to the line R_0.

The imaginary part of the effectiveness function is determined by the polarization part of the intermolecular potential (induction and dispersion interaction) and the imaginary part of electrostatic interactions. The isotropic part of polarization interactions in the Unsold approximation[20] depends on the difference between average polarizability and dipole-moment values in the upper and ground transition states:

$$S_1(i,f,b,v) = \frac{3\pi}{8\hbar v b^5}\left\{\alpha_2\left\{\left\langle V_i\left|\mu_1^2\right|V_i\right\rangle - \left\langle V_f\left|\mu_1^2\right|V_f\right\rangle\right\} + \right.$$

$$+\left[\mu_2^2+\frac{3}{2}\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\alpha_2\right]\left\{\langle V_i\mid\alpha_1\mid V_i\rangle-\langle V_f\mid\alpha_1\mid V_f\rangle\right\}\Bigg\}. \quad (9)$$

Here μ_1 and μ_2 are the dipole-moment functions and α_1 and α_2 are the polarizability functions of absorbing and perturbing molecules; ε_1 and ε_2 are ionization potentials. In case of self-broadening, $\mu_1 = \mu_2$, $\alpha_1 = \alpha_2$, and $\varepsilon_1 = \varepsilon_2$. In terms of semiclassical impact broadening theory[18] in approximation of the straight line paths and moderate collision velocity, the line center shift $\delta(i, f)$ is expressed as

$$\delta(i,f)=\frac{nv}{c}\sum_j\rho(j)\times$$

$$\times\int_0^\infty\left[\sin\left(S_1(b)+\operatorname{Im}S_2(b)\right)\exp\left(-\operatorname{Re}S_2(b)\right)\right]b\,db. \quad (10)$$

When accounting for the dipole–dipole interaction, the imaginary part of the effectiveness function of the 2nd order $\operatorname{Im}S_2$ is

$$\operatorname{Im}S_2^{\text{outer}}(i,f,b,v)=\frac{4}{9}\frac{1}{(\hbar v b^2)^2}\sum_{j'}D(jj'\mid 1)\times$$

$$\times\left\{\sum_{i'}D(ii'\mid 1)\operatorname{Im}\varphi_{11}(k_{ii'jj'})-D(ff'\mid 1)\operatorname{Im}\varphi_{11}(k_{ff'jj'})\right\}. \quad (11)$$

The summarized strength D of the line has been defined in Eqs. (3) and (4). To calculate $\operatorname{Im}S_2$, let us use the mean transition frequency approximation (6), (8):

$$\operatorname{Im}\tilde{S}_2^{\text{outer}}(i,f,b,v)=$$

$$=\frac{4}{9}\frac{1}{(\hbar v b^2)^2}\mu_0^2\left\{\mu_i^2C_i(b,B_i)-\mu_f^2C_f(b,B_f)\right\}. \quad (12)$$

Here functions $C_i(b, B_i)$ and $C_f(b, B_f)$ were calculated by Eq. (6) at $\operatorname{Re}\varphi_{11} = \operatorname{Im}\varphi_{11}$, mean transition frequencies – by Eq. (8). Further calculations of halfwidths and line center shifts for HF and CO were performed using the effectiveness function $\operatorname{Im}\tilde{S}_2^{\text{outer}}(i,f,b,v)$ (12), $\operatorname{Re}\tilde{S}_2^{\text{outer}}(i,f,b,v)$ (7), and $S_1(i, f, b, v)$ (9).

2.1. Vibrational dependence of HF line center shifts and halfwidths in hot and cold bands

Halfwidths of HF–HF lines were calculated with the use of *ab initio*-calculated functions of the dipole moment,[11] the quadrupole moment,[12] and the polarizability.[13] Some molecular constants were taken from Ref. 21. Required matrix elements of the dipole moment, polarizability, and rotational constant were determined through numerical integration. Note, that the calculated parameters significantly vary under the influence of the HF vibrational excitation. For example, the calculated mean dipole moment for the ground state is equal to 1.83 D (which well agrees with the value found experimentally), while at v = 22 it equals to 0.228 D, i.e. is 16.6 times less. The HF molecule polarizability quickly increases up to 1.7 Å^3 at v = 19, which nearly twice exceeds its value (0.78 Å^3) at the ground state. The vibrational excitation of this molecule leads to a sharp increase of the moment of inertia due to increase of the atom vibration amplitude. As a result, the rotational constant significantly decreases: by a factor of 7 at v = 22 as compared to its value at v = 0. The value of the rotational constant B_0 equal to 20.62 cm^{-1}, calculated in this work for v = 0, is in good agreement with the well-known B_0 value equal to 20.96 cm^{-1} (Ref. 21). Thus, vibrational excitation of HF molecule results in strong changes of mean molecular parameters, as well as a significant change of rotational energy spectrum. Evidently, these factors differently affect the line halfwidth, e.g. a decrease in the mean dipole moment leads to a strong its decrease; a decrease of the rotational constant results in a slight its increase and line center shifts, the polarizability increase results in a significant increase of the line shift.

To determine total effect of vibrational excitation, the halfwidths and line center shifts have been calculated. The effect of intermolecular interactions, accompanying the strong vibrational excitation of an absorbing molecule, on the halfwidth and center shifts of HF–HF lines is estimated in Ref. 14, using the polarizability mean values for several vibrational states v = 1, ..., 5 of the HF molecule. In this work, the *ab initio*-calculated polarizability function[13] is used in calculations of the halfwidth and line center shift. The contribution of dipole–quadrupole and quadrupole–quadrupole interactions, as well as a close-range part of the potential into the broadening and shift of HF–HF line centers were estimated as well. Estimations show the contribution to not exceed 1% for transitions to v = 2.

The vibrational dependence of line halfwidths for cold (crosses) and hot (circles) bands is given in Fig. 3.

Calculations show that this dependence is quite complicated: the halfwidth slightly increases (up to 8%) for v = 0, ..., 6; further increasing of the transition energy leads to a 25% narrowing of lines in comparison with lines of the rotational band.

Calculational results for HF–HF line halfwidths for hot transitions v → v + 1 are given in Fig. 3 as well. Calculations of the dipole moment functions have shown that off-diagonal matrix elements of the dipole moment operator $\langle V_i|\mu_1|V_{i+1}\rangle$ (4) of an absorbing molecule are comparable with diagonal ones $\langle V_i|\mu_1|V_{i'}\rangle$ (3) at the vibrational quantum number v > 5; therefore, vibrational dependence of hot-band line halfwidths should be studied. Note, that the narrowing effect for hot-band lines is more clearly pronounced, losses in higher-band halfwidths exceed 50%. As a whole, variations of HF–HF line halfwidths are mainly determined by the behavior of the dipole-moment function.

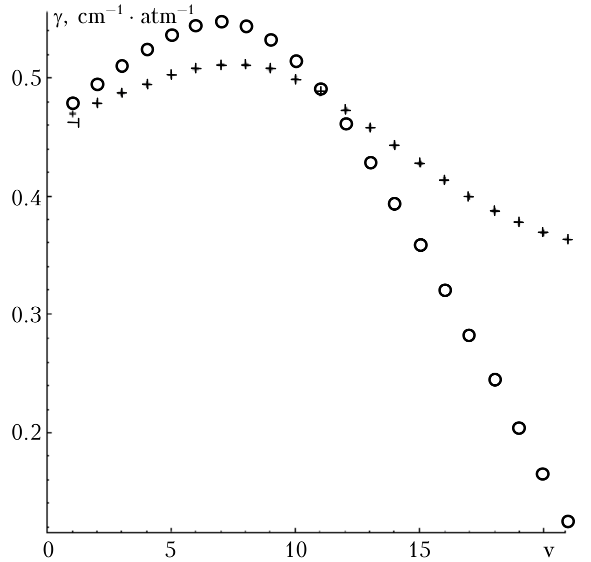

Fig. 3. HF–HF line halfwidths for vibrational bands as functions of the vibrational quantum number v.

The calculational results for line center shifts in cold (crosses) and hot (circles) bands are given in Fig. 4. Estimates of the ratio of the center shift of 0–v bands to those of 0–2 band show the line center shift to increase 3.5 times in the 0–5 band and 24 times in the 0–20 band. Calculational results for line center shifts of hot bands $v_n \to v_n + 1$, $v_n = 1, ..., 21$ are given in Fig. 4 as well. Line center shifts for hot bands vary less due to less polarizability difference $\alpha_f = \alpha_i$ in S_1 (9).

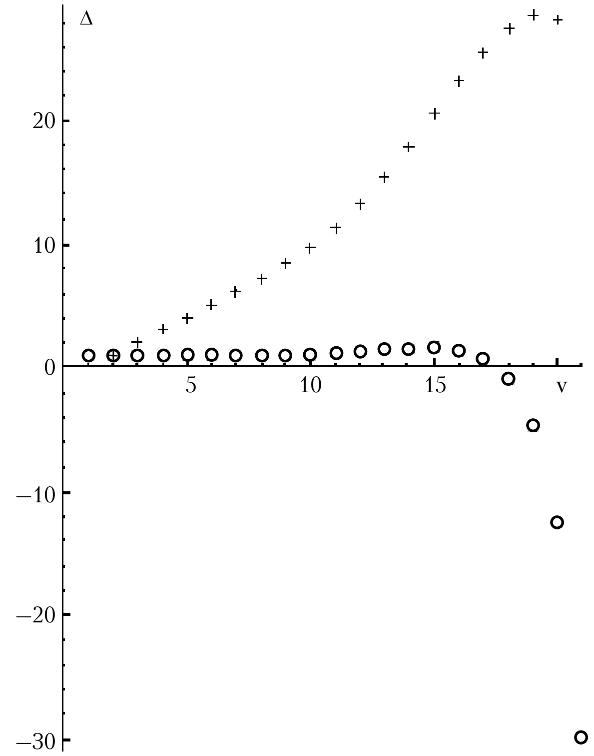

Fig. 4. Relative change $\Delta = \delta_{0-v}/\delta_{0-2}$ of shifts of HF–HF line centers for vibrational bands as a function of the vibrational quantum number v.

As calculations show, the vibrational dependence of the shift *in toto* strongly correlates with of the polarizability function behavior. As a result, negative contribution into line shifts increases tenfold due to increase of the contribution into the line center of the isotropic part of polarization interactions (8). The obtained results are in good qualitative agreement with calculational results[22] for H_2O line center shifts of higher bands.

Hence, the obtained data on center shift variations for HF absorbing lines in case of self-broadening are caused by polarizability function variation, which is clearly pronounced under strong vibrational excitation of the absorbing molecule.

2.2. Vibrational dependence of CO halfwidths and line center shifts in hot and cold bands

In calculations of halfwidths and line center shifts the dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions in $\tilde{S}_2^{\text{outer}}(i,f,b,v)$ (7), (12), as well as isotropic part of induction and dispersion interactions in $S_1(i, f, b, v)$ (9) were taken into account. *Ab initio* calculated functions of dipole[15] and quadrupole moments[16] and the polarizability[17] were used to study the vibration dependence of line relaxation parameters. The rotational constant for v = 0 and some constants for CO molecule were taken from Ref. 21. Matrix elements of dipole and quadrupole moments, the polarizability, and the rotational constant necessary for calculations of relaxation parameters, were determined by the numerical integration.

Note, that the calculated parameters vary significantly under influence of vibrational excitation of the CO molecule. For example, the calculated mean dipole moment for the ground state is equal to –0.12 D (which agrees well with the experimental value), while its value at v = 50 is equal to 1.04 D, i.e. is 8.7 times larger and opposite in sign. The mean quadrupole moment of CO molecule changes from –2.0 at v = 0 to 0.842 at v = 50, i.e. decreases 2.4 times in absolute magnitude (see Fig. 2).

Since the CO molecule has a small dipole moment, its quadrupole moment should be taken into account when calculating halfwidths and line center shifts. As is shown, intramolecular parameters can vary essentially as the vibrational excitation of the molecule increases (the polarizability increases 1.5 times and the rotational constant decreases 2 times). A partial compensation of intramolecular dynamics effects is possible. For example, a decrease of the rotational constant results in an increase of CO–CO lines' halfwidths (by 22% at v = 23 as compared to v = 1); an increase of the mean dipole moment results in decrease of line halfwidths.

To study the total effect of vibrational excitation on relaxation parameters of CO–CO lines, calculations were carried out (Eqs. (1)–(12)) based on the method from Ref. 18 and the mean transition frequency approximation.[14] In general, the vibrational dependence of CO–CO line halfwidths is complicated (Fig. 5): up to $v = 10$ the halfwidth decreases, then up to $v = 50$ it increases by 40% in comparison with its value at $v = 10$. The vibrational dependence of line halfwidths is determined by the behavior of dipole- and quadrupole-moment functions and, in a less degree, by the polarizability and the rotational constant.

Off-diagonal dipole-moment elements have been calculated and their values were shown to be comparable with the diagonal ones at $v > 20$. CO–CO line halfwidths were calculated for cold and hot bands, respectively. Figure 5 shows the calculated line halfwidths for cold (crosses) and hot (circles) bands formed by transitions $0 \to v_n$, $v_n = 1, ..., 50$ and $v_n \to v_n + 1$, $v_n = 1, ..., 49$, respectively.

Note, that the vibration dependence for hot bands is weaker. Probably, this can be related to small variations of the dipole-moment matrix elements under strong vibrational excitation of the CO molecule.

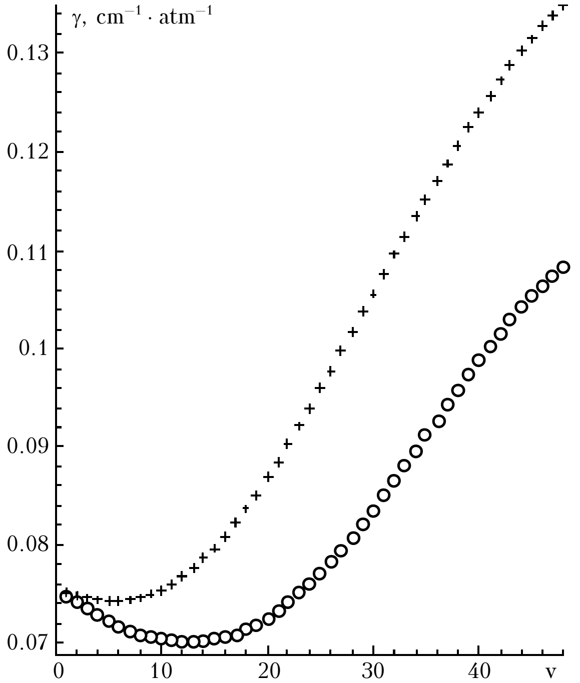

Fig. 5. Halfwidths of CO–CO lines for vibrational bands as functions of the vibrational quantum number v.

Line center shifts for cold (crosses) and hot (circles) CO bands under self-broadening conditions are shown in Fig. 6.

In this case, the vibration dependence of CO–CO line center shifts is mainly determined by the behavior of the polarizability function, though the vibration dependence of the rotational constant and dipole and quadrupole moments also results in a small shift increase. The line center shift in cold bands sharply increases (50 times as much in the 0–50 band as compared to the shift in the 0–2 band), while in hot bands it varies not more than twofold under the influence of vibrational excitation.

Note, that halfwidths of HF–HF (Fig. 3) and CO–CO (Fig. 5) lines, calculated in similar conditions, behave differently: HF–HF lines narrow and CO–CO lines widen with the increase of the vibrational quantum number v. The reason of the difference is in differing bond types in absorbing molecules determining the behavior of functions of dipole and quadrupole moments. The vibration dependence of line center shifts due to behavior of the polarizability function increases monotonically both for HF and CO.

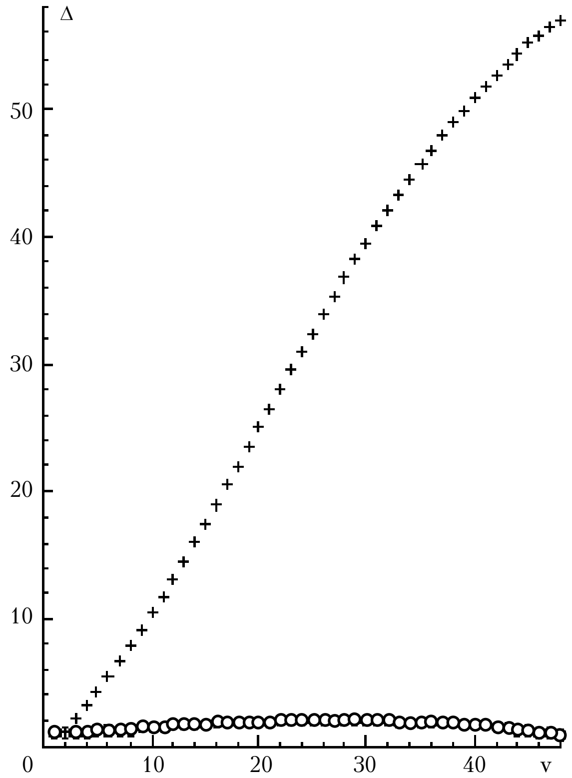

Fig. 6. Relative change $\Delta = \delta_{0-v}/\delta_{0-2}$ of the CO–CO line center shift for vibrational bands as a function of the vibrational quantum number v.

Conclusion

In this work, halfwidths and center shifts for HF–HF and CO–CO lines under strong vibrational excitation of absorbing molecules were calculated for the first time. The approximation, accounting for all basic factors of vibrational excitation, was used in calculations, i.e. variations of the mean dipole moment and the force of the dipole–dipole interaction, the quadrupole moment, the polarizability of the absorbing molecule and the adiabatic effect, as well as the retuning of the rotational energy spectrum. It is necessary to emphasize, that results of *ab initio* calculations were taken as the initial data. Since the HF molecule has a large constant dipole moment and polarizability, the dipole–dipole, induction, and dispersion interactions are important. Dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, and isotropic part of polarization interactions were taken into account for CO molecule. The case of self-broadening of the R_0 line was considered (mean frequencies were chosen just for this line, when the resonance energy exchange between colliding molecules occurs).

The calculations have shown that the vibrational dependence of line halfwidths is mainly determined by the behavior of functions of dipole and quadrupole moments. The vibration dependence of line center shifts is due to variations of the polarizability function. The reliability of the obtained estimates is supported by the comparison with experimentally observed line halfwidths, as well as HF (Refs. 2–5) and CO (Refs. 6–8) line center shifts in low rovibrational bands. Note, that the proposed model of the vibration dependence of spectral lines' relaxation parameters, which uses *ab initio* calculated functions of multipole moments and polarizability, allows:

1) the study of the vibration dependence of halfwidths and line center shifts in diatomic molecules for higher rovibrational bands;

2) a reliable estimation of halfwidth and R_0-line center shift for HF and CO molecules for high vibrational states near the dissociation limit.

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